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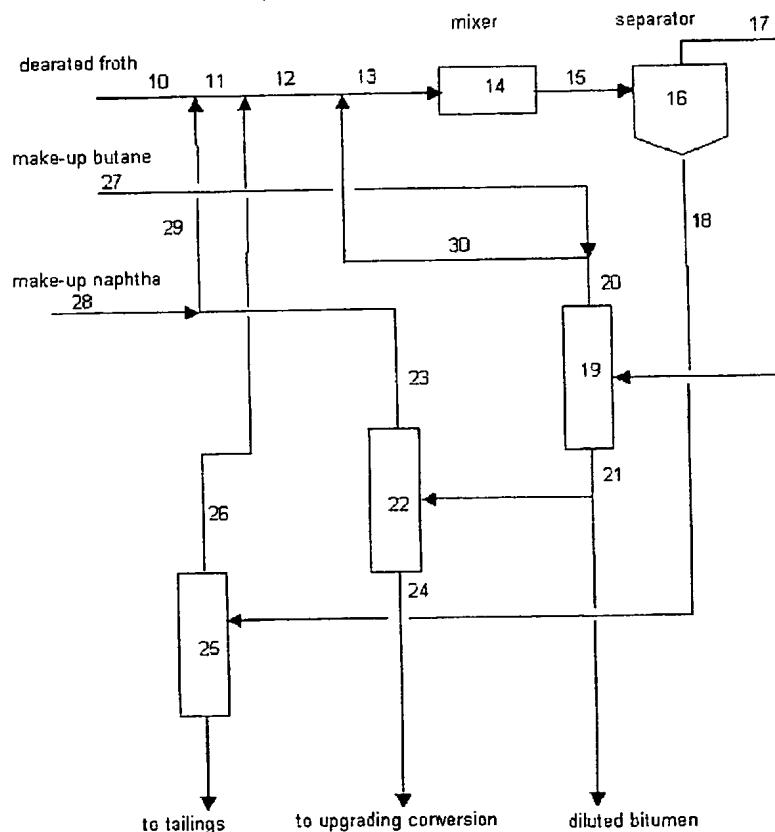
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(54) Titre : PROCEDE DE TRAITEMENT D'EMULSIONS D'HUILES LOURDES AU MOYEN D'UN MELANGE DE NAPHTA ET D'HYDROCARBURE ALIPHATIQUE LEGER

(54) Title: PROCESS FOR TREATING HEAVY OIL EMULSIONS USING A LIGHT ALIPHATIC SOLVENT-NAPHTA MIXTURE



(57) Abrégé/Abstract:

A bitumen-water emulsion is treated with a mixture comprised of a naphtha and a light aliphatic hydrocarbon such as butane. The treatment destabilises the emulsion and results in the removal of most of the water and mineral. The treatment also results in the

(57) Abrégé(suite)/Abstract(continued):

precipitation of some of the asphaltenes present in the bitumen. The degree of deasphalting is easily controlled to make a product of a specified asphaltene content. Since for heavy oils such as Athabasca bitumen, metals such as nickel and vanadium are concentrated in the higher boiling point tail end and are associated with asphaltenes, the removal of asphaltenes reduces the metals content of the product. Depending on the selected concentration of metals and asphaltenes, the treated product may be further upgraded in a range of conversion processes including coking and catalytic hydrocracking units.

Process for Treating Bitumen Emulsions Using Light Aliphatic Solvent - Naphtha Mixture

ABSTRACT

5

A bitumen-water emulsion is treated with a mixture comprised of a naphtha and a light aliphatic hydrocarbon such as butane. The treatment destabilises the emulsion and results in the removal of most of the water and mineral. The treatment also
10 results in the precipitation of some of the asphaltenes present in the bitumen. The degree of deasphalting is easily controlled to make a product of a specified asphaltene content. Since for heavy oils such as Athabasca bitumen, metals such as nickel and vanadium are concentrated in the higher boiling point tail end and are associated with asphaltenes, the removal of asphaltenes reduces the metals content
15 of the product. Depending on the selected concentration of metals and asphaltenes, the treated product may be further upgraded in a range of conversion processes including coking and catalytic hydrocracking units.

Process for Treating Bitumen Emulsions Using Light Aliphatic Solvent - Naphtha Mixture

5 This invention relates to the treatment of bitumen emulsions, to break such emulsions in order to remove water and minerals and to precipitate some of the asphaltene fraction. In a particular preferred embodiment, this invention relates to the treatment of emulsions, particularly bitumen froth, encountered in the extraction of oil from oil sands.

10 **Background of the Invention**

The oil sands located in northern Alberta, Canada contain bitumen with a gravity of approximately 8 API, in concentrations of 6 to 14 wt. %. The Alberta oil sands deposits contain an estimated 400 billion cubic metres of bitumen in place, 15 and form one of the world's largest known sources of oil.

There are major commercial operations based on the mining of the oil sands. However, the costs of extracting, treating and upgrading bitumen are high. It is therefore desirable to improve the process steps in the production of crude oil from such oil sands. In addition the concentration of mineral matter and metals, such as 20 vanadium and nickel, restricts the choice of processes which may be used in upgrading the bitumen to synthetic crude oil.

Techniques for the extraction of bitumen from mined oil sands are well known in the industry and include hot or cold water flotation, water-solvent mixtures, and solvent extraction. An established commercial method for the processing of Alberta 25 oil sands is the Clark hot water extraction process. After mining, this extraction process treats the oil sands with steam, hot water and caustic soda to recover the bitumen in the form of a complex bitumen-water-solids-air mixture called bitumen froth.

A typical composition of the bitumen froth is approximately 60 wt. % bitumen, 30 30 wt. % water and 10 wt. % minerals. The water contains various salts derived

from the connate water in the oil sands formation. The minerals include a wide range of sand and clays inherent in the oil sands formation, with particle sizes down to submicron levels. Also present in the bitumen are naturally occurring surfactants, which can be activated by chemical reaction with the caustic soda used in the extraction process. The composition of this froth mixture is prone to the formation of tight emulsions, which makes the removal of water and mineral a difficult task.

Most of the water and minerals must be removed before the bitumen can be treated in a refinery-type upgrading facility. The removal of water and minerals is described in this document as "bitumen cleaning" or "froth treatment".

One widely used method of bitumen cleaning first deaerates the froth, then dilutes the bitumen with a naphtha to reduce the density relative to water and also reduce the viscosity of the oil phase. This permits separation of the phases in standard separation devices. In this method, naphtha (manufactured as a product in the upgrading of the bitumen) is added to the deaerated froth in solvent-to-bitumen ratios typically in the range of 0.6 wt/wt. The mixture of deaerated froth and solvent is treated in devices such as centrifuges, inclined plate separators or hydrocyclones, to separate an aqueous phase from a naphtha-diluted bitumen. The composition of the "clean" mixture of bitumen and naphtha resulting from this treatment is typically 2 to 5 wt. % water and 0.3 to 1 wt. % mineral. On a bitumen basis, this is about 3 to 6 wt. % water and 0.6 to 1.5 wt % mineral.

It has been disclosed in U.S. patent 5,876,592 and US 6,214,213 to combine deaerated bitumen froth with a paraffinic solvent such as heptane, hexane or a natural gas condensate which is predominantly paraffinic. The patent teaches that this can result in a product with a water and mineral content which is considerably lower than that from the conventional naphtha dilution process.

Description of the Invention

The invention achieves a dry, low mineral product and in addition provides an easily controlled means for the removal of a predetermined amount of the

asphaltene fraction, resulting in a partially upgraded product with reduced levels of asphaltenes and metals such as nickel and vanadium.

According to the invention, the emulsion is treated with a naphtha and one or more C₃ or C₄ aliphatic hydrocarbons. In this disclosure, C₃ or C₄ aliphatic hydrocarbons and mixtures thereof will collectively be called "light solvent". The preferred light solvent is propane or butane, or mixtures thereof, i.e., light solvents which do not have any double or triple bonds. "Butane" includes n-butane and isobutane, and mixtures thereof.

The process of the invention can be used to treat froths, such a bitumen froth or secondary froths from a Clark process of oil extraction from oil sands. The froth is first deareated then mixed with a naphtha and a light solvent as defined above.

When the invention is used to treat bitumen froth in a typical integrated oil sand processing facility, both the naphtha and the light solvent are conveniently obtained on-site, from the bitumen upgrading process which follows the oil sand extraction process. The light solvent need not be pure, and can be in a mixture of light hydrocarbons as will be the case where it is recovered as an overhead stream from a hydrotreater naphtha stabilizer. Mixed isomers need not be separated, and C₃ components and C₄ components need not be separated from one another. Depending on the conversion process and overall configuration of the upgrader, as well as marketing arrangements, there is usually a surplus of butane produced by the upgrading process beyond that which is required for blending into the synthetic crude oil. It is therefore particularly convenient to use the excess butane as the light solvent. In any event, because of the high vapour pressure of the light solvent, expected losses are very low, as very high recoveries can be obtained in standard distillation equipment.

The naphtha used in this invention is any conveniently available naphtha. Conveniently, it can be obtained from the primary conversion process, for example from a coker, or it can be a saturated material from the hydrotreaters which often follow the primary step. Such naphthas have an API gravity of about 55 to 65 and a boiling range in degrees Farhenheit of 100 Initial boiling point to 450 Final boiling point. Naphtha from a delayed coker tends to have a high sulphur content (for

example about 17000 ppmw) and high nitrogen content (for example about 150 ppmw. When hydrotreated the sulphur and nitrogen contents are reduced to as low as 200 ppmw and 1 ppmw respectively.

5 The light solvent can be obtained from the upgrader hydrotreater stabilizer. Generally, therefore, all of the solvents used in the process are available on-site at an integrated oil sands treatment facility.

Description of the Drawings

10 The invention will be described further with respect to the appended drawings, in which:

Figure 1 is a schematic diagram of apparatus suitable for the practice of the present invention

15 Figure 2 is a triangle diagram showing percentages of light solvent (which in this case is butane), naphtha and bitumen. The triangle diagram has an operating line. The area above the line in the diagram shows operating conditions where sufficient water can be removed according to the invention from the bitumen to give a bitumen product with 0.5% or less water.

20 Figure 3 is a graph plotting the percentage of asphaltene in the bitumen product against the total solvent to bitumen ratio, for a naphtha-light solvent blend according to the invention (line A) and for butane alone (line B).

Detailed description of the invention

In Figure 1, an emulsion of bitumen and water, for example a deearated froth
25 from a source such as a Clark hot water process plant enters through line 10. A make-up naphtha enters as stream 28 and combines with the recycled naphtha recovered by distillation, stream 23 to form the stream 29. The total naphtha, stream 29, then combines with the incoming deearated froth to form stream 11. A mixture of naphtha and butane, stream 26, recovered from vacuum stripper 25, is added to

become stream 12. The light solvent, for example, butane enters from line 30 and combines with the mixture which is then fed as stream 13, to the mixer 14. The mixed material, stream 15, is fed to a conventional phase separator 16, which may be a centrifuge, inclined plate or other known phase separation apparatus for
5 bitumen froth treatment. The phase separator produces a hydrocarbon phase (stream 17) and an aqueous phase (stream 18). The hydrocarbon phase (stream 17) is fed to a distillation column 19, where the light solvent is recovered overhead as stream 20. The recovered light solvent is combined with a make-up stream 27, which is obtained from a stabilizer in the upgrader. The combined light solvent stream joins
10 the feed to the mixer 14. The separator 16 underflow, stream 18, is fed to a vacuum column to recover naphtha and light solvents which are recycled as stream 26 to the join the feeds to the mixer 14. The bottoms from the vacuum column, 25 is routed to the tailings management system. The asphaltene content of stream 21 is monitored,
15 and can be adjusted to a desired level by controlling the solvent inputs through lines 29 and 30.

There are several alternative processing options for the bottoms, stream 21, from the light solvent recovery column 19. Stream 21 may be fed to the naphtha recovery/upgrader feed preparation column 22. A part of the stream 21 may be routed to storage as a diluted bitumen where there is a market for such a product.
20 The column 22, produces an overhead naphtha, stream 23, which combines with a make-up naphtha, stream 28, and the combined stream, joins the dearrated froth, stream 10. The bottoms of column 22 is stream 24, which is routed to the conversion unit of the upgrader.

The ratios of the two solvents, each expressed relative to bitumen is desirably
25 chosen in a range which achieves the desired product quality, in terms of a bitumen product with not more than a stated amount of water. Thus, when the desired product quality is bitumen containing less than 0.5% water, the percentages of naphtha and of light solvent should be chosen from the area above the operating line in Figure 2. If the desired product has a different dryness (for example, less than 1%
30 water, or less than 0.75% water, the operating line would be in a different position on Figure 2. Such an operating line can be determined empirically for any desired dryness of product. (product quality).

Bitumens can be deasphalting by light solvent alone. However, as shown by line B in Figure 3, a small change in the solvent to butane level gives rise to a very large change in the percentage of asphaltenes in the product. Thus a small variation in the solvent to bitumen ratio, caused for example by a variation in the amount of 5 froth entering the process, can lead to a major change in the asphaltene content of the bitumen exiting the process. This may make the bitumen unsuitable for downstream processing.

The invention solves this problem by using a solvent which is a mixture of naphtha and light solvent. As is seen from line A in Figure 3, changes in the total 10 solvent to bitumen ratio cause a much more gradual change in the asphaltene content of the product than is the case when the light solvent (butane) is used alone (line B in Figure 3).

The presence of the naphtha makes control of the degree of deasphalting easier as the sensitivity to solvent to bitumen ratio is lower than with a single light 15 aliphatic solvent. This is shown in figure 3. In order to maintain the desired target of asphaltene and metal concentration in the product bitumen, the degree of asphaltene precipitation can be controlled by adjustment in either the light solvent to naphtha ratio or the overall solvent to bitumen ratio. The slope of the line showing the degree of deasphalting as a function of the solvent to bitumen ratio is influenced 20 by the percentage of naphtha in the total solvent mixture. A higher ratio of naphtha to light solvent gives a gentler slope and allows easier control of the degree of deasphalting. This flexibility gives both the process designer and the operator a wide degree of freedom.

The ratios of the two solvents expressed as on a wt/wt basis to bitumen can 25 vary from 0.2 to 1.0 for naphtha and 0.6 to 2.0 for the light solvent. A typical combination of solvent ratios (based on bitumen) is 0.85 w/w for butane and 0.3 w/w for naphtha, where an asphaltene percentage of 13-14% in the final product is desired.

The process is carried out at a pressure where the light solvent, in the 30 amounts present, does not flash off as a gas. Thus, the process is carried out at greater than atmospheric pressure. The required pressure will vary, as will be

evident to one skilled in the art, with the particular light solvent or solvents and naphtha used and with the operating temperature.

The temperature at which the process is carried out ranges from about 25 to about 120 degrees Celsius, with the preferred temperature range being about 50 to 5 120 degrees Celsius. For example, in an extraction plant, which uses the Clark hot water process operating at around 85 degrees Celsius, the invented process may be operated at that temperature.

The light solvent and naphtha are mixed with the emulsion to be treated. The mixture is fed to a separation vessel, such as a settler or inclined plate separator, or 10 a separation device such as a hydrocyclone where the emulsion-solvent mixture breaks into two phases, one of which contains most of the water and minerals, and some precipitated asphaltenes. The remaining (oil) phase contains the light solvent, naphtha and a clean, partially deasphalted bitumen.

The treated bitumen is very low in minerals, water and soluble salts such as 15 chlorides, and contains reduced amounts of asphaltenes and metals. Typical concentrations of mineral and water in the treated bitumen are usually 0.1 or lower weight percent for each component. The low concentrations of minerals, salts and water, and the reduced amounts of asphaltenes make the bitumen suitable for subsequent processing by a wide range of upgrading processes from cokers to 20 catalytic hydrocrackers

The light solvent and the naphtha can be recovered from the oil phase by distillation either together or separately. Both are recycled. The remaining bitumen is then fed to the conversion unit of the upgrader.

An optional configuration is to strip the light solvent for recycling and to allow 25 the remaining naphtha-bitumen blend to leave the plant as a final pipelinable product, in the case where a market exists for such a product.

By selecting the appropriate light solvent/naphtha composition and solvent-to-bitumen ratio, a controlled amount of asphaltenes can be precipitated. The removal of a portion of the asphaltene fraction contributes to reduction of the viscosity of

bitumen product, thus reducing amount of solvent needed to make bitumen pipelineable.

The tailings stream is preferably vacuum stripped to recover the light solvent and the naphtha and is then routed to tailings processing.

5 The invention offers the opportunity to retrofit an existing oil sand facility based on naphtha treatment. The retrofit is accomplished by adding a new froth treatment plant and a stripper section to recover the light solvent by distillation. The bottoms product from the stripper contains naphtha and may be stored in the existing diluted bitumen tanks. No changes need to be made to the existing diluent recovery
10 system, since this is based on the distillation of naphtha. Because the plant can be run on naphtha only, start-up and shutdowns are easily carried out, using the naphtha, with the light diluent added after the upgrader is up and producing it. Therefore, there is no need for significant amounts of high-pressure storage facilities for the light solvent.

15

Examples

The invention will now be described by reference to particular examples.

Continuous flow-through pilot plant runs were made using apparatus configured as in Figure 1 (except that recycle lines 23, 26 and 30 were not present)
20 to treat typical deaerated bitumen froth from a commercial Clark hot water process carried out near Fort McMurray, Alberta, Canada. The composition of the deareated froth was: bitumen 61.4 wt. %, water 28.5 wt. %, and solids 10.2 wt. %. The solvent to bitumen ratios were as follows: butane to bitumen 1.0 w/w, naphtha to bitumen 0.3 w/w, for a total solvent to bitumen ratio of 1.3 w/w.

25 All samples were analysed by the Dean and Stark procedure. Pentane insolubles and microcarbon tests were carried out on the bitumen in the froth and product.

Experiments were carried out using both commercially pure n-butane and naphtha obtained from a commercial oil sands plant as solvents. The naphtha used had a density at 25°C of 0.7588 and sulphur content of 1.67 wt. %.

5 Examples 1 - 3

Runs were carried out using as solvent a butane-naphtha mixture with solvent ratios (based on bitumen) of 0.85 w/w for butane and 0.3 w/w for naphtha. Results were as follows:

Butane/Naphtha solvent			
	Example #1	Example #2	Example #3
10 Froth feed, kg/min	0.337	0.270	0.270
Butane feed, kg/min	0.193	0.184	0.213
Naphtha feed, kg/min	0.0579	0.0552	0.0639
Product rate, kg/min	0.438	0.407	0.401
15 Tails rate, kg/min	0.150	0.102	0.146
Temperature, °C	78	80	80
Water content based on bitumen, wt%	0.10	0.07	0.09
Ash content based on bitumen, wt%	0.10	0.08	0.07
Asphaltenes content, wt%	13.7	13.2	11.7
20 Maltenes recovery, wt%	96.2	98.3	97.7
Overflow flux, mm/min	32.6	28.7	30.8

Examples 4 - 6

25 Runs were carried out using butane as solvent, with no naphtha present.

Results were as follows:

	Example #4	Example #5	Example #6
Froth feed, kg/min	0.393	0.360	0.315
Butane feed, kg/min	0.211	0.220	0.181
Naphtha feed, kg/min	0	0	0
Product rate, kg/min	0.433	0.401	0.354
Tails rate, kg/min	0.171	0.180	0.141
Temperature, °C	82	83	81
Water content based on bitumen, wt%	0.46	0.26	0.15
Ash content based on bitumen, wt%	0.20	0.09	0.04
Asphaltenes content, wt%	17.2	9.6	8.0
Maltenes recovery, wt%	96.2	94.4	93.7
Overflow flux, mm/min	31.7	27.5	26.4

These results are plotted as line B in Figure 3.

Example 7

An operating line was developed for a desired product quality (less than 0.5% water in the product), by doing a series of runs with different solvent ratios and the same bitumen froth, and noting the amount of water in the product. The runs were
5 entered on the graph which is Figure 2. (The numbers on Figure 2 are the individual run numbers, which do not correspond to the run numbers in Examples 1-6). A "best-fit" line separating solvent ratios that gave 0.5% water or less from those which gave more than 0.5% water was then drawn on the graph of Figure 2. From this graph, one can determine the ratios of bitumen, light solvent and naphtha which can
10 be utilized if one seeks a bitumen product having less than 0.5% water. Ratios in the area of the graph above and to the left of the line are suitable to obtain such a result.

It is understood that the above disclosure is illustrative only, and that variations will be evident to one skilled in the art. Therefore, it is intended that the claims be read to include such obvious variations.

What is claimed is:

1. A method of treating a bitumen froth emulsion, which comprises:
 - (a) deaerating the emulsion,
 - 5 (b) contacting the deaerated emulsion in a phase separator with naphtha and with a light solvent selected from the group of C₃ and C₄ hydrocarbons, at a pressure sufficiently high so that the light solvent does not flash off, whereby the emulsion breaks into a water phase and an oil phase,
 - 10 (c) recovering light solvent from the oil phase, the remaining oil phase after such recovery being the bitumen product of the process,
 - (d) monitoring said bitumen product for its asphaltene content, and
 - 15 (e) controlling the asphaltene content in the bitumen product to a desired value by adjusting during the contacting step at least one of the ratio of naphtha to light solvent and the ratio of the total of naphtha and light solvent to bitumen.
2. A process as claimed in claim 1, in which the light solvent is a paraffin.
3. A process as claimed in claim 1 in which the light solvent is butane.
4. A process as claimed in any of claims 1-3, in which the contacting step is carried out at a temperature of from 25 to 120 degrees Celsius.
- 20 5. A process as claimed in any of claims 1-3, in which the contacting step is carried out at a temperature of from 50 to 120 degrees Celsius.
- 25 6. A process as claimed in any of claims 1-5, in which the ratio of naphtha to bitumen in the contacting step is from 0.2 to 1.0 wt/wt, and the ratio of light solvent to bitumen in the contacting step is from 0.6 to 2.0 wt/wt.

7. A method as claimed in any of claims 1-6, in which the water content of the product is less than 0.5% by weight of the weight of bitumen present.
9. A method as claimed in any of claims 1-8, including the step of separating out naphtha from said resulting oil phase.
- 5
10. A method as claimed in claim 9, in which the separated naphtha is recycled to the phase separator.

Application number / numéro de demande: 2435113

Figures: 3

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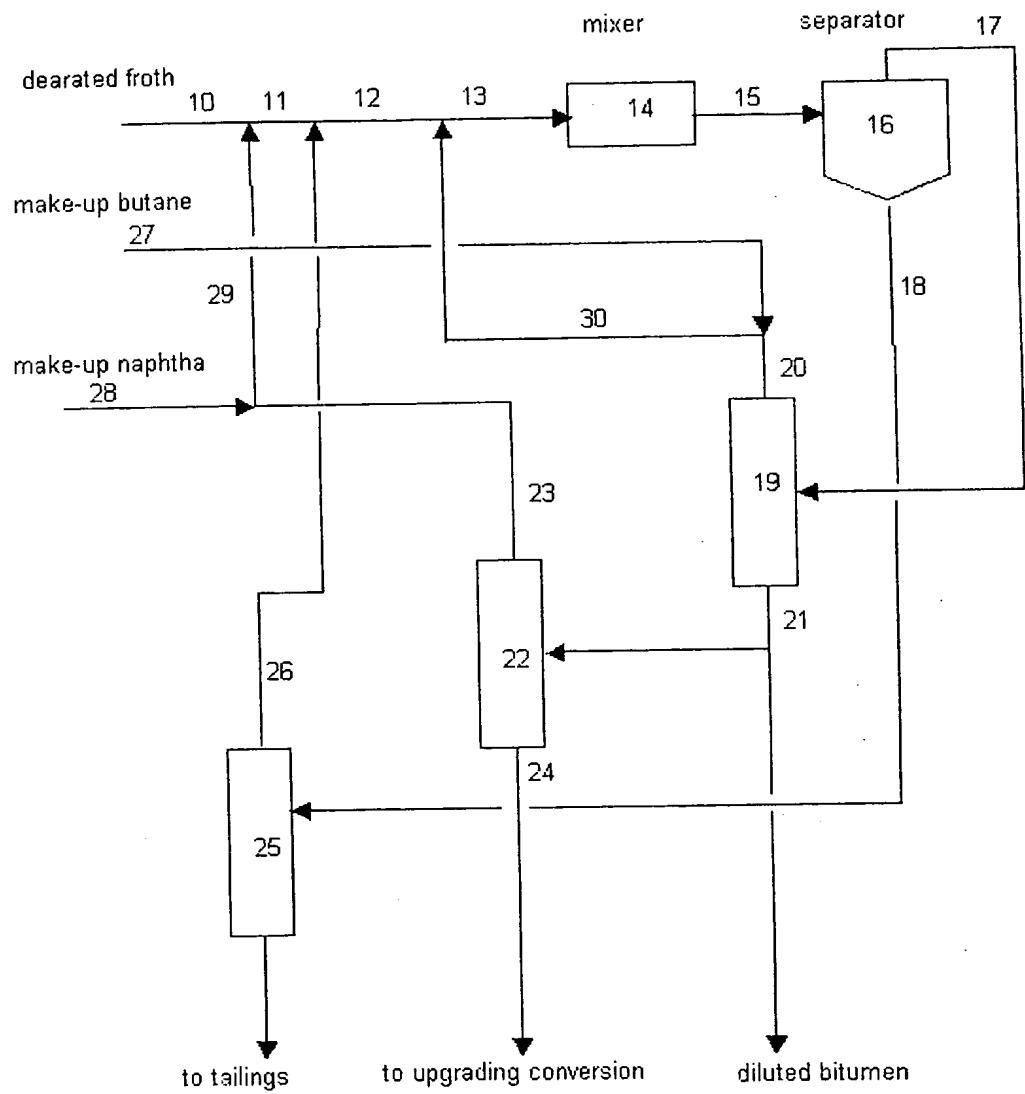


Figure 1

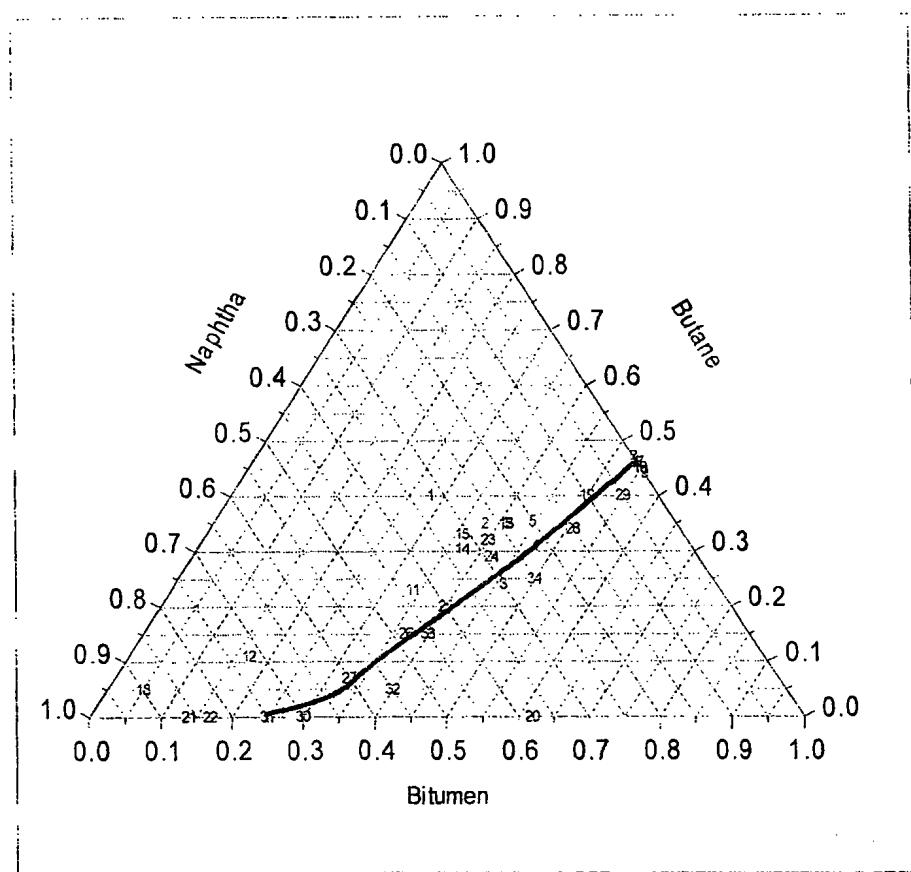


Figure 2